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Abstract

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Finite Potential Window of High Conductivity

by

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**Potential Dependence of the Conductivity of Poly(3-
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David Ofer and Mark S. Wrighton*

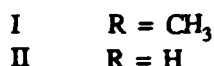
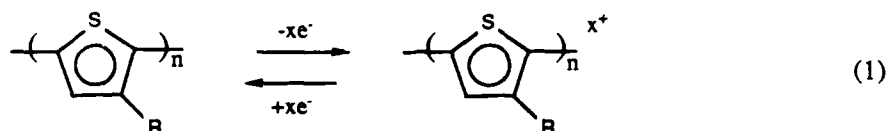
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Abstract

Poly(3-methylthiophene), I, on Pt microelectrodes shows reversible oxidation in liquid SO₂/electrolyte, and accompanying oxidation of I are large changes in its conductivity. By using liquid SO₂/0.1 M [(n-Bu)₄N]PF₆ as the solvent/electrolyte system it is possible to study the conductivity vs. potential for very positive potentials, to ~+2.5 V vs. Ag. Over the large potential range explored, I has a broad maximum in conductivity at ~+0.9 V vs. Ag, and a more positive excursion results in substantially lower conductivity. The width of the region of high conductivity is ~1.3 V, substantially wider than that for polyaniline. Results for polythiophene, II, in SO₂/0.1 M [(n-Bu)₄N]PF₆ are similar to those for I. Results for I and II show that it is possible to sufficiently depopulate the highest occupied electronic bands of I and II to render them non-conducting, as suggested by theory.

We wish to communicate the potential dependence of the conductivity of thiophene-derived polymers I and II confined



to Pt microelectrodes. The data show a broad maximum in conductivity as suggested by theory which shows a finite width for the highest occupied electronic bands.¹ The width of the region of high conductivity and the maximum conductivity are related, because the bandwidth of the highest occupied band is a measure of the degree of delocalization in the system and can be roughly correlated with carrier mobility in the band.¹ It is known that oxidation of I or II, equation (1), leads to a dramatic increase in conductivity.² However, electrochemical studies of I and II^{2,3} failed to reveal maxima in conductivity, possibly because chemical degradation of I and II occurs at positive potentials in the media used. The medium used for our new studies is liquid SO₂/0.1 M [(n-Bu)₄N]PF₆ at -40°C. It has been demonstrated that liquid SO₂/electrolyte is a medium that allows observation of highly oxidized species.⁴

Previous work in this laboratory has shown that polyaniline does have a potential dependent conductivity in

aqueous H_2SO_4 ⁵ or in the solid electrolyte polyvinylalcohol/ H_3PO_4 ,⁶ showing a well-defined maximum in conductivity at $\sim +0.3$ V vs. SCE and a region of high conductivity ~ 0.6 V wide. Bandwidths of polyaniline,⁷ and polythiophene^{1,8} have been calculated, but the results depend strongly on the structures assumed for the polymers. Such theoretical calculations should give reliable trends in bandwidth for structurally similar polymers. The calculations^{1,7,8} suggest that a large fraction of the electrons in the highest occupied band might be electrochemically accessible in a number of polymers.

Arrays of eight individually addressable Pt microelectrodes (~ 2 μm wide, ~ 50 μm long, and ~ 0.1 μm high), separated from each other by ~ 1.2 μm ,^{3,5,9} can be coated and "connected" with I or II by anodic polymerization of the thiophene monomer in $\text{CH}_3\text{CN}/0.1$ M $[(n\text{-Bu})_4\text{N}]\text{PF}_6$ as described by us³ and earlier by others.¹⁰ Two microelectrodes connected with a redox-active polymer can be used to determine the potential dependence of the conductivity of the polymer. At a fixed potential difference (drain voltage, V_D) between the two microelectrodes, the magnitude of the drain current, I_D , between the electrodes changes as the potential of the polymer, V_G , is changed.^{3,5,9} Thus, I_D - V_G curves reveal the potential dependence of the conductivity, as reflected by I_D , of the polymer.

Figure 1 shows the scan rate dependence for cyclic voltammetry of I on a Pt microelectrode array in liquid

SO₂/0.1 M [(n-Bu)₄N]PF₆ at -40°C. Integration of the voltammogram indicates reversible removal of 9×10^{-8} moles of e⁻'s per cm² of area covered by polymer. We estimate that the oxidation process shown corresponds to removing one to two electrons per four repeat units of the polymer. At potentials negative of 0.6 V vs. Ag, the features of the voltammogram correspond to those previously reported in other solvent/electrolyte systems.^{2,3,10} In the region of more positive potential, new features, anodic and cathodic peaks at ~1.2 V and ~1.0 V vs. Ag, respectively, are observed. The cyclic voltammetry over the entire region shown is qualitatively different than previously reported. Further work is required to establish the nature of the chemical changes accompanying the reversible removal of charge.

Figure 1 also shows the I_D-V_G characteristic in liquid SO₂/0.1 M [(n-Bu)₄N]PF₆ at -40°C for an adjacent pair of Pt microelectrodes connected with I. Negative of 0.6 V vs. Ag, the I_D-V_G characteristic corresponds to that previously observed in both liquid and solid electrolyte systems.^{3,11} The new finding is that the conductivity of I significantly declines as the polymer is further oxidized, as reflected in the small values of I_D at very positive values of V_G. The polymer resistances at -0.2, +0.9, and +2.0 V vs. Ag are $>10^{10} \Omega$, $<100 \Omega$, and $\sim 10^4 \Omega$, respectively. The region of high conductivity is ~1.3 V, much wider than for polyaniline.^{5,6} The hysteresis evident in the I_D-V_G curve

is scan rate independent in the range 10^1 - 10^3 mV/sec, and correlates with hysteresis in the cyclic voltammetry. Hysteresis in the properties of conducting polymers upon redox cycling has been explained as resulting from changes in polymer structure.¹² The behavior of II made by anodic polymerization of 2,2'-bithiophene on Pt microelectrodes is very similar to that of I, except that the region of high conductivity is more narrow (~1.0 V width) and the maximum conductivity is somewhat less.

The observation of lowered conductivity in highly oxidized polythiophenes is consistent with theoretical expectations^{1,8} and is similar to observations made for polyaniline.^{5,6} Considering the data for polyaniline,^{5,6} I, and II, it does appear that the polymer with the greatest conductivity, I, also has the widest region of conductivity. Earlier, studies of the potential dependence of the conductivity of polypyrrole have been reported for a limited potential range.^{9,13} We are currently investigating polypyrrole and its derivatives over a wider potential range to determine the width of the region of conductivity in these cases. Our findings have important practical implications relating to the use of conducting polymers I and II as electronic materials in batteries and microelectronic devices, since the polymers are shown to have a finite potential window where high conductivity occurs.

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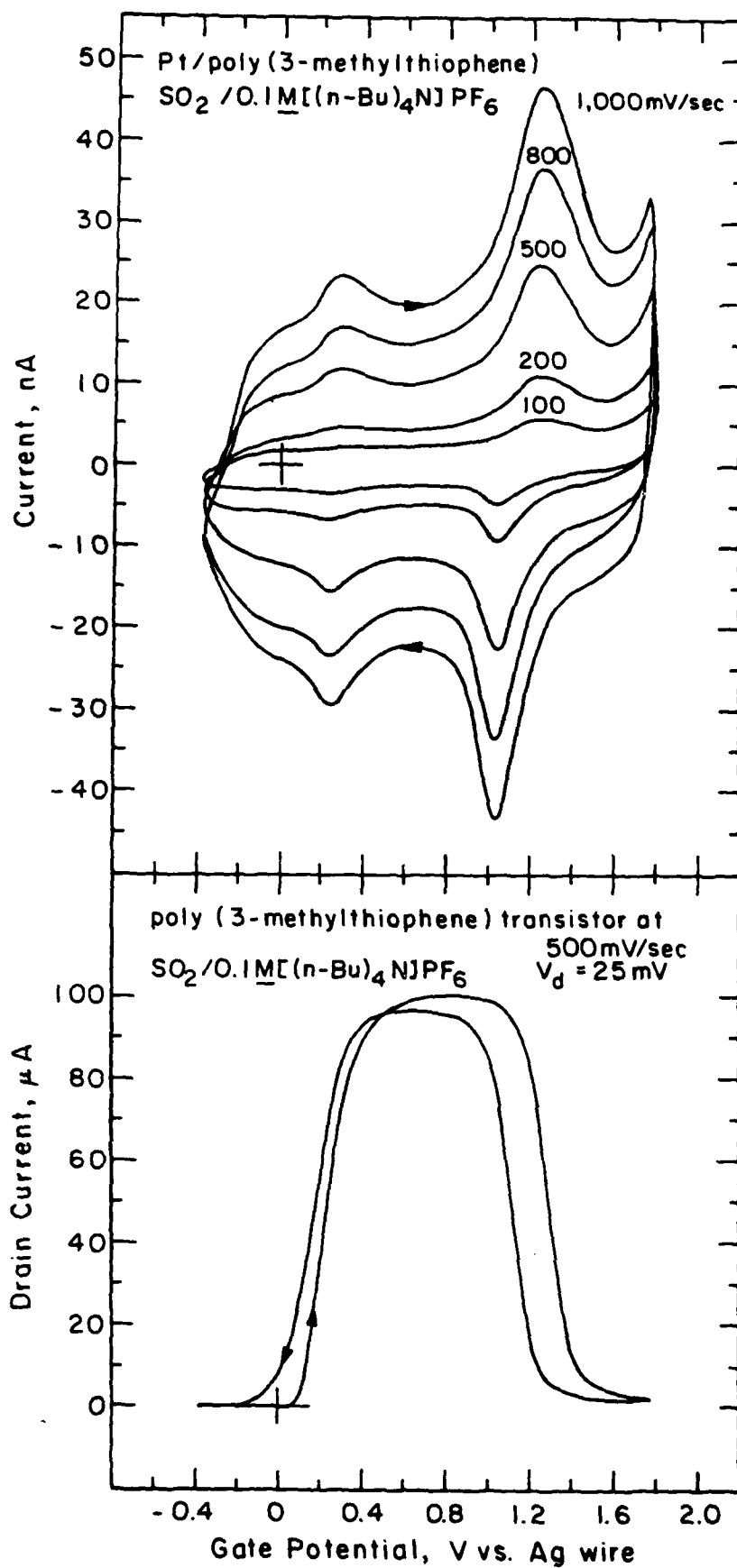
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Figure Caption

Figure 1. Top: Sweep rate dependence for cyclic voltammetry of I on three adjacent Pt microelectrodes in $\text{SO}_2/0.1 \text{ M}$ $[(n\text{-Bu})_4\text{N}]\text{PF}_6$. Bottom: I_D - V_G characteristic for an adjacent pair of the microelectrodes coated with I for which cyclic voltammetry is shown. In the region of maximum I_D , the current is partially limited by the significant resistance of the microelectrode leads ($\sim 200 \Omega$). All data are for solutions at -40°C .



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